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Kinetic Modeling of Combustion Characteristics of Real Biodiesel Fuels

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Abstract

Biodiesel fuels are of much interest today either for replacing or blending with conventional fuels for automotive applications. Predicting engine effects of using biodiesel fuel requires accurate understanding of the combustion characteristics of the fuel, which can be acquired through analysis using reliable detailed reaction mechanisms. Unlike gasoline or diesel that consists of hundreds of chemical compounds, biodiesel fuels contain only a limited number of compounds. Over 90% of the biodiesel fraction is composed of 5 unique long-chain C_{18} and C_{16} saturated and unsaturated methyl esters. This makes modeling of real biodiesel fuel possible without the need for a fuel surrogate. To this end, a detailed chemical kinetic mechanism has been developed for determining the combustion characteristics of a pure biodiesel (B100) fuel, applicable from low- to high-temperature oxidation regimes. This model has been built based on reaction rate rules established in previous studies at Lawrence Livermore National Laboratory. Computed results are compared with the few fundamental experimental data that exist for biodiesel fuel and its components. In addition, computed results have been compared with experimental data for other long-chain hydrocarbons that are similar in structure to the biodiesel components.

Introduction

Biodiesel is produced by a transesterification process of soy and rapeseed oil, and contain mixtures of a few long-chain alkyl esters. While running an engine on pure biodiesel B100 may need more research and development due to biodiesel's low volatility, it is easier to blend it with conventional diesel up to 20% (B20). However, it is important to understand the combustion characteristics of a pure biodiesel in order to understand the combustion behavior of its blends. Detailed chemical kinetic mechanisms are great tools to investigate biodiesel's engine combustion behavior, as well as the effects of blending with conventional fuels. To simulate combustion behavior and capture fuel effects, one needs surrogate mixtures to represent real fuels, due to the complexity of fuels. Unlike gasoline or diesel, which consist of hundreds of chemical compounds, biodiesel fuels contain only a limited number of compounds. Biodiesel derived from the most common sources, such as soybean and rapeseed oil, is composed of five unique long-chain C_{16} and C_{18} saturated and unsaturated methyl esters. The typical composition of biodiesel derived from two different sources is shown in Table 1, along with the component's carbon number and the number of unsaturated carbon bonds in the component. For example, methyl oleate ($C_{18}:1$) contains eighteen carbon atoms with one $C=C$ bond. [1]

The limited number of components makes representation of biodiesel in simulation possible without

the need for a fuel surrogate. Since the C_{18} chain methyl esters are most abundant in biodiesels, we have begun to develop a detailed reaction mechanism for the kinetically simplest C_{18} fraction in biodiesel – methyl stearate. The structure of the molecule is shown in Figure 1. Development of a detailed reaction mechanism for methyl stearate (also called methyl heptadecanoate), along with validation of that mechanism, is described in this article.

Table 1. Average composition (%) of biodiesels.

Ester	Soybean derived	Rapeseed derived
Methyl palmitate ($C_{16}:0$)	6-10	4.3
Methyl stearate ($C_{18}:0$)	2-5	1.3
Methyl oleate ($C_{18}:1$)	20-30	59.9
Methyl linoleate ($C_{18}:2$)	50-60	21.1
Methyl linolenate ($C_{18}:3$)	5-11	13.2

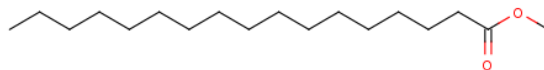


Figure 1. Molecular structure of methyl stearate.

Several literature studies focused on smaller methyl esters. Oxidation of methyl butanoate ($C_5:0$) has been the subject of several papers. Fisher et al. [2] developed a detailed reaction mechanism for the oxidation of methyl butanoate. Recently, Metcalfe et al. [3] studied the

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oxidation of methyl butanoate and ethyl propanoate in a shock tube. Dooley et al. [4] further revised a detailed reaction mechanism based on the work of Fisher et al. for methyl butanoate. Herbinet et al. [5] recently developed a detailed-kinetics mechanism for methyl decanoate, which was the largest methyl ester available prior to this work. In addition, several studies also proposed various surrogates to model real biodiesel. Herbinet et al. [5] used a mixture of methyl decanoate and *n*-heptane. Naik et al. [6] proposed a three-component surrogate mixture of methyl butanoate, methyl crotonate, and *n*-dodecane to simulate biodiesel.

Despite the availability of several biodiesel surrogates and their reaction mechanisms, the experimental data on real biodiesel are scarce. Most experimental studies have focused on smaller methyl esters like methyl butanoate [7] and methyl crotonate [8]. Marchese et al. [9] studied the ignition time of bio-ester fuel droplets in microgravity and showed that methyl decanoate and methyl dodecanoate are better surrogates for commercial soy oil methyl esters than methyl butanoate, in agreement with conclusions of Fisher et al. [2] and Gail et al. [10]. One of the very few experimental studies on real biodiesel is by Dagaut et al. [11]. They performed an experimental study of the oxidation of a rapeseed-oil methyl ester in a jet-stirred reactor at 1-10 atm, over the temperature range 800-1400 K. They measured species profiles for major species. To model the experiments, they used *n*-hexadecane as a surrogate and found satisfactory predictions except that they could not predict the early production of CO₂ observed in the experiments.

Good knowledge of the kinetics of the reactions of biodiesel fuels at both high and low temperatures is necessary to perform reliable simulations of ignition, combustion and emissions in homogeneous charge compression ignition (HCCI) and diesel engines. Modeling of the oxidation of methyl stearate provides a better understanding of the chemistry of methyl-ester combustion. It can also be used as a single-component surrogate for commercial biodiesel fuels. In this work, a detailed chemical-kinetics mechanism has been developed and used to study the oxidation of methyl stearate, which is a more direct representation of biodiesel fuel than other smaller methyl esters. This model is compared with the available data using rapeseed-oil methyl ester experiments in a JSR [11] and shock-tube ignition of smaller alkanes like *n*-heptane [12] and *n*-decane [13].

The ultimate future goal will be to extend the methyl stearate mechanism to include kinetics for unsaturated C₁₈ methyl esters and the remaining compounds listed in Table 1.

Mechanism Development

As a base for the development of methyl stearate mechanism in this work, we started with the detailed

chemical-kinetics mechanism for oxidation of *n*-alkanes up to *n*-hexadecane, which was developed recently at Lawrence Livermore National Laboratory (LLNL) [14]. As shown in Figure 1, methyl stearate could be considered as a combination of primary radicals of *n*-hexadecane and methyl formate. Therefore, it is efficient to begin the mechanism development work with the complete base of the *n*-hexadecane mechanism. This comprehensive base mechanism contains 25 reaction classes pertaining to high-temperature (Classes 1 to 9) and low-temperature oxidation (Classes 10 to 25) of hydrocarbons, as previously reported by Curran et al. [15].

We then added the reactions for all 25 classes for methyl esters. Though the reactions were similar in type to those in the methyl decanoate mechanism of Herbinet et al. [5], here we employed the same rate-rules as those used by Westbrook et al. [14] for large *n*-alkane mechanism. For the nine classes of reactions pertaining to the high-temperature portion of the mechanism, reactions involving all saturated methyl esters, starting from methyl acetate and up to methyl stearate, were included in the mechanism. However, to reduce the complexity of the mechanism and limit the number of species in the mechanism, we limited the reactions for the low-temperature portion of the mechanism to the fuel of interest, i.e., to methyl stearate. We also removed all the low-temperature kinetics for *n*-alkanes from *n*-octane to *n*-hexadecane. This method is justified since there is negligible fuel decomposition at low temperatures and in the negative-temperature-coefficient (NTC) region of interest. Therefore, it is possible to avoid reactions of smaller non-fuel species in that temperature regime.

In addition, we had to make one modification to the existing rate-rules for the reaction classes involving the addition of molecular oxygen to parent radicals and to QOOH (Class 10 and Class 22 in [14]). Reactions I to IV in Table 2 display the overall scheme of low-temperature oxidation, leading to chain branching that is required for auto-ignition of fuels in the NTC region. Here R• is a methyl ester radical analogous to the alkyl radical for *n*-alkanes. Reaction I (Class 10) and Reaction III (Class 22) are almost without barrier in the forward direction. However, the reverse of those reactions (i.e., dissociation) is also very fast, such that the equilibrium decides the fate of chain branching and significantly contributes to the NTC behavior in alkanes. We effectively increased the well-depth for the O₂ addition to the parent methyl stearate radical and subsequent QOOH species (Reaction I and III) by 2 kcal/mol by increasing the activation energy in the dissociation direction. Results shown in the next section are from using these updated rate rules.

Table 2. A brief scheme of hydrocarbon oxidation at low temperatures that leads to chain branching.

No.	Reaction
I	$R\cdot + O_2 = RO_2\cdot$
II	$RO_2\cdot = Q\cdot OOH$
III	$Q\cdot OOH + O_2 = \cdot OOQOOH$
IV	$\cdot OOQOOH \Rightarrow \text{chain branching}$

Results and Discussion

The kinetics mechanism for methyl stearate developed in this work has been validated against two different types of experiments: (1) Jet-stirred reactor (JSR) data using a rapeseed-oil methyl ester from Dagaut et al. [11] at 10 atm, 1 s residence time, at equivalence ratios (ϕ) of 0.5 and 1 for temperatures from 800 K to 1170 K; and (2) auto-ignition in shock tubes at an equivalence ratio of 1, for 13 and 50 bar pressures, measured for *n*-heptane and *n*-dodecane, respectively. The initial temperatures for the auto-ignition experiments ranged from 660 K to 1300 K. The Perfectly Stirred Reactor and Closed Homogeneous Reactor models from the CHEMKIN-PRO [16] software have been used for simulations of the experiments, using the detailed kinetics mechanism.

Comparisons of predicted species profiles using methyl stearate to those measured for the rapeseed-oil methyl ester in the JSR for ϕ of 1 are shown in Figure 2 and Figure 3. Profiles for O_2 , CO, and CO_2 are captured very well by the model. Predicted H_2 and CH_4 concentrations are lower than those observed above 1000 K. Minor olefin products ethylene, propylene, and 1-butene are also captured very well by the model, whereas 1-pentene and 1-hexene are slightly overpredicted. Comparisons of predicted species profiles to those measured in a JSR for an equivalence ratio of 0.5 are shown in Figure 4 and Figure 5. Predictions for all major products and minor olefin products agree well with the data. The agreement is better than those seen for stoichiometric conditions.

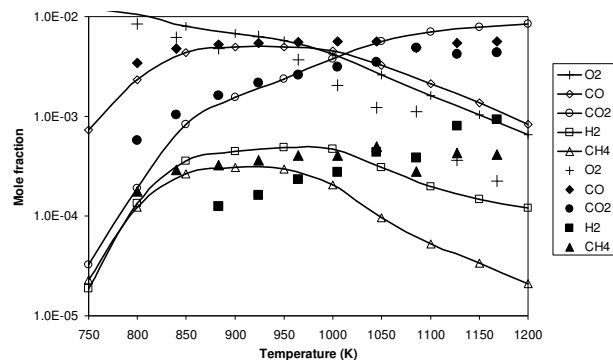


Figure 2. Comparison of predicted major species profiles to those measured in JSR by Dagaut et al. [11] at 10 atm, 1 s residence time, and equivalence ratio of 1.

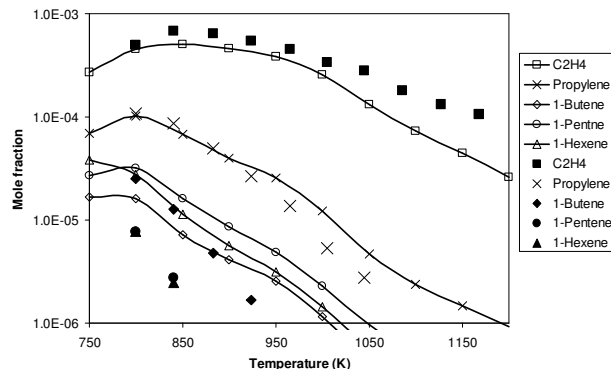


Figure 3. Comparison of predicted minor species profiles to those measured in JSR by Dagaut et al. [11] at 10 atm, 1 s residence time, and equivalence ratio of 1.

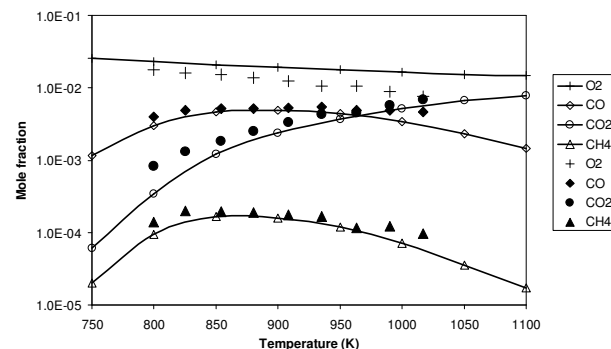


Figure 4. Comparison of predicted major species profiles to those measured in JSR by Dagaut et al. [11] at 10 atm, 1 s residence time, and equivalence ratio of 0.5.

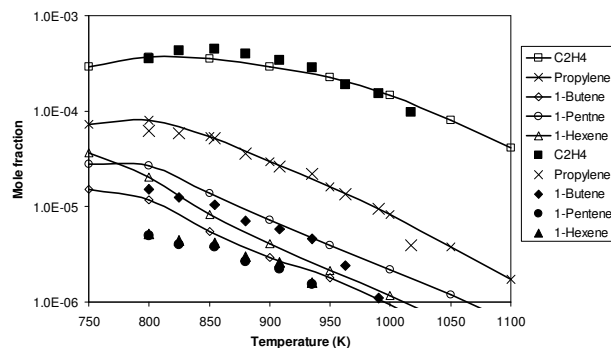


Figure 5. Comparison of predicted minor species profiles to those measured in JSR by Dagaut et al. [11] at 10 atm, 1 s residence time, and equivalence ratio of 0.5.

The methyl stearate mechanism successfully captures all major and minor species profiles measured in the JSR using the real biodiesel. The model also captures the early production of CO_2 at lower temperatures that was not

captured using *n*-hexadecane [11], which typically results from the ester part of the fuel component [5]. Therefore, methyl stearate appears to be a good surrogate for biodiesel, even though it does not contain any of the unsaturated compounds that are found in the highest concentrations in real biodiesel.

Due to the lack of any ignition data for biodiesel or for methyl stearate, we compared the ignition time of methyl stearate to those measured for *n*-heptane and *n*-decane. Westbrook et al. [14] recently showed using the mechanistic predictions that auto-ignition time for all *n*-alkanes from *n*-heptane to *n*-hexadecane is very similar, within a factor of two. Herbinet et al. [5] also showed that ignition qualities of methyl decanoate are very similar to those of *n*-heptane and *n*-decane. Based on these studies, we expect methyl stearate to show similar auto-ignition

behavior as *n*-heptane and *n*-decane, at least within a factor of two from the measured ignition time. Comparisons of auto-ignition times of a stoichiometric methyl stearate/air mixture to those measured in shock tubes for *n*-heptane at 13 bar [12] and for *n*-decane at 50 bar [13] are shown in Figure 6. As expected, predictions are very similar to the data. We can also see that predictions of methyl stearate agree well with those of methyl decanoate using the previously published methyl-decanoate mechanism [5]. Also shown in Figure 6 are the predicted auto-ignition times for *n*-heptane and *n*-decane at 13 bar and 50 bar respectively using the Westbrook et al. mechanism. These predictions confirm that all *n*-alkanes and all long-chain methyl esters that have carbon chain longer than *n*-heptane have similar ignition qualities.

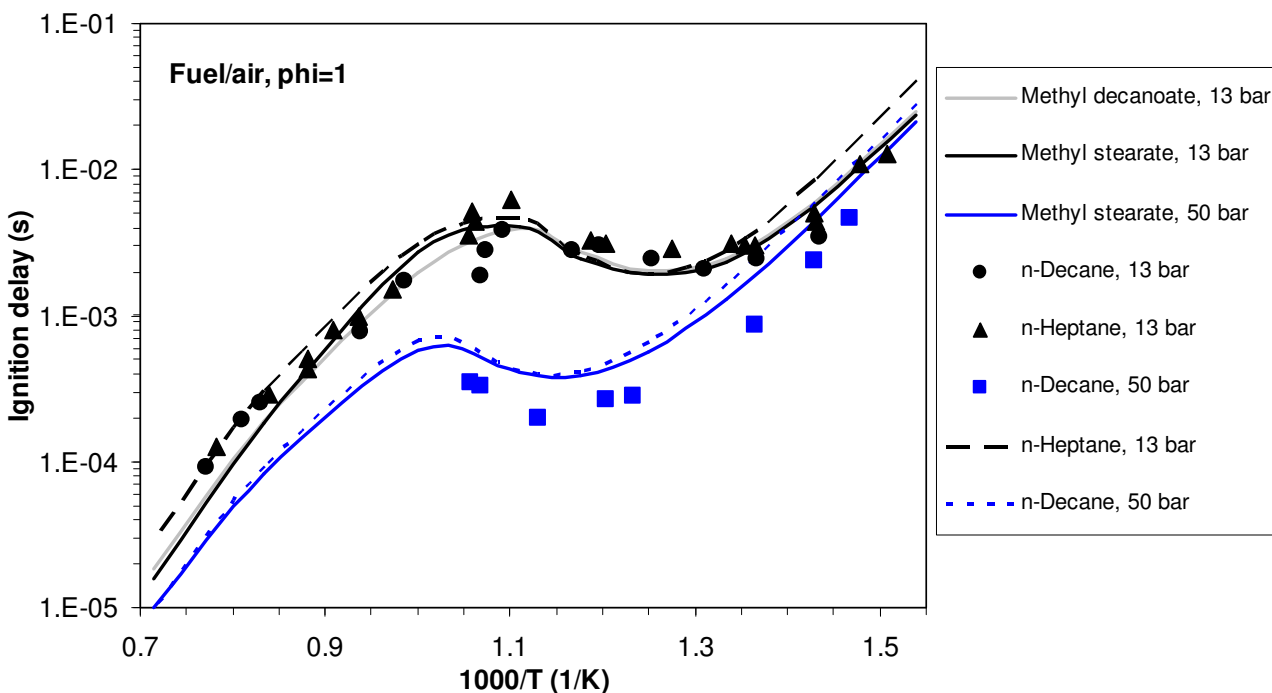


Figure 6. Comparison of predicted autoignition times of methyl stearate to those measured for other stoichiometric fuel/air mixture of *n*-heptane [12] and *n*-decane [13]. Predictions using literature mechanisms for methyl decanoate (Herbinet et al. [5]) and *n*-heptane [14] at 13 bar, and *n*-decane [14] at 50 bar are shown.

Conclusion

A detailed chemical-kinetics mechanism for the oxidation of methyl stearate has been developed for determining the combustion characteristics of biodiesel, applicable over all temperature regimes. This mechanism has been built using reaction-rate rules established in previous studies for *n*-alkanes. Predictions are compared with data from the few fundamental experiments available for biodiesel and for other long-chain hydrocarbons. The model is found to be in good agreement with these data. Methyl stearate is also found to be a good surrogate for biodiesel.

Acknowledgements

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